MODELING THE PROCESS OF UNSTEADY ONE-DIMENSIONAL DIFFUSION OF AN AGGRESSIVE MEDIUM

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The unsteady one-dimensional diffusion of an aggressive medium across the thickness of a long cylindrical shell is investigated. Data on the concentration of the medium on the outer surface of the shell and the diffusion coefficient are given in the form of piecewise-constant functions of time. The distribution of concentration of the medium across the thickness of the shell and the time-dependent integrally average concentration for shells 1 and 0.5 cm thick are obtained. The concentration of the aggressive medium in the shell is calculated up to a period of five years. The results obtained are compared with calculations for a continuous concentration of the medium at the boundary and the diffusion coefficient as functions of time. Based on the Rabotnov kinetic theory of creep and long-term strength, a way to predict the long-term properties of structural elements in a aggressive medium is shown.

Introduction

The operation of real structures can take place in a wide variety of conditions and media often aggressive to some extent in relation to the material of a structure. These media can be natural, technogenic, or mixed. The individual aggressive components of these media can diffuse into the volume of a material and enter into a physical and/or chemical interaction with it. This interaction changes the service properties (dielectric, thermophysical, and physicomechanical) of the material and of the structure as a whole.

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In the overwhelming majority of practically important cases, the diffusion penetration of the active components of a medium into a material occurs under varying external conditions (temperatures and concentrations of the aggressive medium). These variable external conditions, in which diffusion takes place, change the diffusion coefficient and concentration of the aggressive medium on the permeable boundary. At some moment of time, a change in external conditions can change the nature of mass transfer, i.e., the sorption can be replaced by desorption.

Since the 1970s, a large number of scientific works on the interaction of corrosive media with materials (mainly metal alloys) and structural members have been published. A wide review of the works is given in [1]. The processes of interaction of moisture with polymer composite materials were studied, for example, in [2-5]. Models of two-phase moisture sorption, a model with time-dependent diffusion, a two-phase material model, and models of relaxation and convection of anomalous diffusion were considered in [2]. In [3], the curves of creep and inverse creep were approximated by the Boltzmann–Volterra linear integral equation, with the use the principle of moisture-time analogy. In [4], the physicomehanical aspects of interaction in a polymer composite/water vapor system and the effect of moisture transfer on the decreasing interlaminar shear strength in basalt- and glass-fiber plastics are considered. The correlation between the kinetic parameters of moisture sorption and the reduced interlaminar strength is shown, and a diffusion model of moisture transfer in specimens of polymer composite materials investigated. It is shown in [5] that, to describe the kinetics of moisture transfer in specimens of polymer composite materials types of damage, the Langmuir model should be preferred, in which the kinetics of the relative change in mass is related to the separation of water into bound and mobile components.

In contrast to the abovementioned investigation, we consider nonstationary external conditions of action of an aggressive medium on the material of a shell in combination with a nonstationary time-dependent distribution of diffusion coefficient.

The concentration distribution of a corrosive medium in a body in time and space has a significant effect on the mechanical, physical, chemical, electrical, and other characteristics of its material. Therefore, the problem on the diffusion kinetics of aggressive components of a medium in a continuum under variable external conditions and diffusion characteristics of the material is undoubtedly urgent.

1. Problem Statement and Initial Data

Let us consider the diffusion process of an aggressive medium in a long cylindrical shell of radius R and thickness $H(H \ll R)$. At a sufficiently large ratio of shell radius to its thickness, this process, with a high degree of accuracy, can be represented as one-dimensional diffusion into a flat plate of thickness $H(H \ll R)$. This flat plate "is" an element of the cylindrical shell located along its generatrix. Let us introduce a coordinate x across the plate thickness (x = 0 and x = H denote the inner and outer surfaces, respectively, of the shell.)

Let us divide each annual cycle with variable diffusion-sorption parameters into N = 12 monthly intervals, so that it will be possible to assume, with a high degree of accuracy, that the diffusion coefficient $D_i = \text{const}$ and the concentration at the boundary $C_{si} = c(x = H, t) = \text{const}$ in each of them. The parameters D_i and C_{si} are independent of each other, and their numerical values are specified in each interval. Such a piecewise constant approximation (within the scale of one month) allows one to take into account, with a high degree of accuracy, the multiple oscillatory nature of the external conditions (concentrations at the boundary, Fig. 1) and diffusion parameters within one year and make a prediction for several years. Reducing the duration of piecewise-constant time intervals, one can take into account all features of changes in the external natural conditions, which increases the accuracy of results of the problems being solved. Therefore, in contrast to the known approximation of natural conditions with the help of harmonic functions [6] (within the scale of several years), the piecewise constant representation of real factors used offers advantages.

Let us consider a one-dimensional unilateral diffusion into a cylindrical shell of thickness H. One surface of the shell (the boundary x = H) is permeable to an aggressive medium, and sorption and desorption occurs through it, but the other surface (x = 0) is impenetrable.



Fig. 1. Piecewise constant concentrations C_s on the boundary x = H (---) and the diffusion coefficient D (----) vs. time t; t is the end time of an *i*th interval.

Interval	1	2	3	4	5	6	7	8	9	10	11	12
Duration of interval, days	30	28.25	31	30	31	30	31	31	30	31	30	31
$D \cdot 10^5$, cm ² /days	0.4	0.5	0.8	1.7	2.5	3.4	4.6	4.42	3.55	3.1	1.0	0.4
C_{si} ,%	0.4	0.8	1.2	4	4	6	5	8	7	6	2	0.8

As an example, let us analyze the development of the diffusion process in time t using the initial data given in Table 1. The piecewise-constant relations for the concentration $C_s(t)$ at the boundary x = H and the diffusion coefficient D(t) are presented in Fig. 1.

The end time of an *i* th month interval coincides with the time of beginning of the (i+1)th interval.

The purpose of is study is to estimate the concentration c(x, t) of the aggressive medium in the shell and its integrally average

$$c_m(t) \equiv \frac{1}{H} \int_0^H c(x, t) dx$$

2. Calculation of Characteristics of Diffusion Process in Shells of Thickness $H_1 = 1$ cm and $H_2 = 0.5$ cm over One Year (12 Intervals)

To calculate the concentration distribution of a corrosive medium in the cross section of a shell in time, the well-known parabolic diffusion equation [7]

$$\frac{\partial c}{\partial t} = D(t) \frac{\partial^2 c}{\partial x^2} \quad , \quad c = c(x, t) \tag{1}$$

with the initial and boundary conditions

$$c(x, 0) = 0, \quad \frac{\partial c}{\partial x}(0, t) = 0, \quad c(H, t) = C_s(t)$$
⁽²⁾

was used.

The solution of Eq. (1) with conditions (2) was carried out numerically by the method of finite differences [8]. In accordance with the problem statement, on each *i* th interval, the parameters C_{si} and D_i take constant values according to the data of Table 1 and Fig. 1. The results obtained at the end of the *i* th interval were used as initial conditions on



Fig. 2. Concentration c vs. the coordinate $\overline{x} = x/H$ at different moments of time t for the shells 1 (1, 6, 12) and 0.5 cm thick (1a, 6a, 12a).



Fig. 3. The integrally average concentration c_m vs. time t for shells 1 (----) and 0.5 cm thick (---).

the (i+1)th interval. Thus, the calculation was carried out for the period of one year (12 intervals) for shells of thickness $H_1 = 1$ cm and $H_2 = 0.5$ cm.

The concentration distributions *c* along the dimensionless coordinate $\overline{x} = x/H$ at the instants of time corresponding to the ends of the first, sixth, and 12th intervals are shown In Fig. 2. While diffusion fronts in the shells have not yet completely filled their entire cross section and have propagated to a small depth, the diffusion process is the same (the impenetrable second boundary is still far away), concentration distributions are the same for these shells, and their plots along the dimensionless coordinate are similar.

The relations $c_m(t)$ over one year are presented in Fig. 3. It is seen that the integrally average concentration in the 1-cm-thick shell is half that in the 0.5-cm-thick one.

We should note that, within each interval (with $D_i = \text{const}$ and $C_{si} = \text{const}$), the concentration distribution c(x, t) varies smoothly in time t (with a continuous derivative). In passing to the next interval (with other parameters $D_{i+1} = \text{const}$ and $C_{s(i+1)} = \text{const}$), a knee in the relation c(x, t) (jump in its derivative) occurs at the time t of transition from the i th to the (i+1)th interval. In the relation $c_m(t)$, a jump at the time of transition from i th to the (i+1)th interval arises. For first few intervals (as an example), these relations are shown in Fig. 4 and 5. Such local changes of the characteristics of diffusion process are explained by the given piecewise constant initial data. The results of a numerical analysis of the relations in the vicinity of the transition point of intervals showed that the greatest effect on the local changes in the characteristics of the diffusion process exerted the piecewise constant relation of the concentration on the boundary C_{si} . Without disturbing the characteristic trends and taking into account the real continuous change in the natural initial data



Fig. 4. Concentration c(x = 0.95, t) on time t at a distance of 0.05 cm from the surface, plotted for the first three intervals by months.



Fig. 5. The integrally average concentration c_m vs. time t, plotted for the first three intervals by months.

of the diffusion process, the smoothed curves, without local kinks and jumps at the points of transition from one interval to the next one, will be presented further.

A reduction in the preset concentration at the boundary in a certain (i+1)th time interval, compared with that in the *i* th time interval, reduces the concentration in the near-boundary region, which corresponds to the desorption processes of material from the shell. This happens in the 11th and 12th intervals, in which significantly lower values of C_s and D than in the previous ones are specified. As a result, the relation $c_m(t)$ in the 11th and 12th intervals is a decreasing function of time (see Fig. 3).

3. Calculation of One-Dimensional Nonstationary Diffusion in Shells of Thickness $H_1 = 1$ cm and $H_2 = 0.5$ cm over Five Years (60 Intervals)

Let us consider a nonstationary diffusion in shells of thickness $H_1 = 1$ cm and $H_2 = 0.5$ cm during five years at a piecewise-constant time-dependences of the diffusion coefficient D(t) and concentration C_p at the boundary x = H (on condition that the boundary x = 0 is impermeable). The condition of complete repetition of the initial data for $C_s(t)$ and D(t) within each year is assumed.



Fig. 6. Concentration c(x) of medium in the shell 0.5 cm thick at the end of each year (number at the curves).



Fig. 7. Integrally average concentrations $c_m(t)$ for shells of thicknesses $H_1 = 1 \text{ cm}(---)$ and $H_2 = 0.5 \text{ cm}(---)$.

The calculation is similar to that in Sect. 2, and its results are presented in Figs. 6 and 7. As an example, the concentration distributions of the aggressive medium in the shell with $H_2 = 0.5$ cm at the end of each year is shown in Fig. 6. The maximum value of its concentration increases in time with a decreasing speed and shifts into depth of the shell.

At moments of time different from those shown in Fig. 6, concentrations of the medium in the shell material in its near-boundary regions can be high (for example, similar to the concentration distribution along the thickness coordinate for the 6th interval, see Fig. 2).

In Fig. 7, the integrally average concentrations $c_m(t)$ for the shells of thicknesses $H_1 = 1$ cm and $H_2 = 0.5$ cm over the period of five years are shown. These distributions are quasi-periodic.

4. Determination of the Relations c(x, t) and $c_m(t)$ at a Continuous Diffusion Coefficient D(t)

It is of interest to approximate the piecewise-constant diffusion coefficient D(t) by a continuous function and to obtain the relations c(x, t) and $c_m(t)$ for it.

Let us transform the parabolic diffusion equation (1) assuming that the function D(t) is continuous. To this end, we introduce a modified time Θ as follows:



Fig. 8. The concentration c(x) for intervals 1, 6, and 12 for a shell 1 cm thick obtained using the modified $(---, \cdots)$ and real (---) time. Explanations in the text.

$$\Theta = \int_{0}^{t} D(t) dt.$$
(3)

As a result, we obtain that

$$\frac{\partial c}{\partial \Theta} = \frac{\partial^2 c}{\partial x^2} \quad . \tag{4}$$

The principle of modified time is widely known (see, for example, [6, 9]) and is used in various forms to simulate long-term, including nonstationary, diffusion processes. In the current paper, this principle is employed in form (3).

The analytic form of the continuous function D(t) is determined by interpolating the piecewise constant timedependent diffusion coefficient D with the use of the Lagrange interpolation polynomial [10]

$$L(x) = \sum_{i=0}^{n} y_i l_i(x)$$

where the basic polynomials $l_i(x)$ are

$$l_i(x) = \prod_{\substack{j=0\\j\neq i}}^{j=n} \frac{x - x_j}{x_i - x_j}$$

Here, x_i and x_j are the given values of argument at the nodal points through which the interpolation graph has to pass; y_i are the given values of the function at the nodal points.

Calculations showed that the a polynomial of degree n = 12 gave absolutely exact values at the interpolation nodes, but allowed significant deviations of vibratory nature between the nodes. To increase the interpolation accuracy over the entire annual period, an interpolation polynomial of degree n = 18 was employed, namely

$$D(t) = \sum_{i=0}^{18} D_i t^i$$
(5)

First, using Eq. (4), we obtained the function $c(x, \Theta)$, which was then transformed into the relation c(x, t) by using Eqs. (3) and (5).



Fig. 9. The integrally average concentration c_m vs. time t obtained using the modified $(--, \cdots)$ and real (--) time.

The calculated relations c(x, t) and $c_m(t)$ for three relations D(t) are presented in Figs. 8 and 9. The solid lines correspond to concentrations for the initial piecewise constant diffusion coefficient D, and the dashed and dotted lines correspond to the D(t) interpolated by Eq. (5) on the beginnings and ends, respectively, of the steps,.

5. Prediction of Long-Term Properties

One of the variants of theories for predicting the long-term properties of materials and structural members in creep under the action of aggressive media can be the Rabotnov kinetic theory of creep and long-term strength [11]. Similar studies based on this theory were also carried out in [12-15]. Further, the general method for determining the characteristics of long-term strength in the presence and absence of an aggressive medium is expounded.

The kinetic equation of damage in the absence of a failure front has the form [16]

$$\frac{d\omega(t)}{dt} = A \left[\frac{\sigma_0}{1 - \omega(t)} \right]^n f(c_m(t)), \quad \omega(0) = 0, \quad \omega(t^*) = 1,$$
(6)

where σ_0 is the nominal stress, ω is the degree of damage, t^* is the time to failure; A and n are material constants; $f(c_m(t))$ is an increasing function satisfying the equality $f(c_m(0)) = 1$. Integrating Eq. (6), the following equation for determining the time to failure t^* , considering the action of an aggressive medium, is obtained:

$$t_{0}^{*} = \left[\left(n+1 \right) A \left(\sigma_{0} \right)^{n} \right]^{-1} = \int_{0}^{t} f \left(c_{m} \left(t \right) \right) dt , \qquad (7)$$

where t_0^* is the time to failure in the absence of an aggressive medium.

Equations (6) and (7) relate the mechanical characteristics and the time to failure in creep to the physicochemical processes caused by diffusion of an aggressive medium. As a function $f(c_m)$ with one material constant, either of the following ones can be considered:

$$f(c_m) = \exp(b_1 c_m), \quad f(c_m) = 1 + b_2 c_m,$$

where b_1 and b_2 are constants to be determined from experiments on long-term strength on structural members subjected to the action of an external aggressive medium (see, e.g. [17]). It follows from relation (7) that aggressive media decrease the time to failure, because $f(c_m) > 1$ at $c_m > 0$.

Conclusions

In this work, the solution of the problem on nonstationary one-dimensional diffusion of an external medium in the material of a cylindrical shell over one to five years was found.

Calculations of the diffusion process were carried out in two ways: by the method of finite differences and using a continuous time-dependent diffusion coefficient determined utilizing Lagrange interpolation polynomials. The integrally average concentration c_m as a function of time t (intervals) over five years was obtained. It is established that the concentration c(x, t) as a function of the coordinate x and the integrally average concentration $c_m(t)$ at a piecewise constant D(t) are located inside the interval determined by using the interpolation functions of D(t). Based on the Rabotnov kinetic theory of creep and long-term strength, a method for predicting the long-term properties of materials and structural members subjected to the action of an aggressive medium is presented.

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